



Potential of visible and near-infrared reflectance spectroscopy for the determination of rare earth elements in soil



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ABSTRACT

The simple and rapid determination of rare earth elements (REE) in soil is essential for the assessment of their environmental and health risks. Inductively coupled plasma-mass spectrometry (ICP-MS) and -emission spectrometry (ICP-ES) are most commonly used for the determination of REE. However, both require complex sample preparation. In this study, we investigated the potential of visible and near-infrared (Vis-NIR) reflectance spectroscopy for determining REE in soil. We collected 130 soil samples near REE mines. Their Vis-NIR spectra, which range from 350 to 2500 nm, were measured after air-drying and grinding in the laboratory. Partial least squares regression (PLSR) was selected to calibrate the spectra and REE contents measured by ICP-MS. The results showed that the absorption features of REE were not distinct in the soil spectra, such as for Nd at 798 nm, which were masked by soil components, particularly by iron oxides because they have overlapping spectral features with REE. However, when using the spectra in the 400–1000 nm range, good or reasonable accuracy [$R^2 > 0.5$ and residual prediction deviation (RPD) > 1.4] was observed for La, Pr, Nd, Sm, and total light REE (Σ La–Eu excluding Pm) because their spectral features could be identified by PLSR calibration. The spectral pretreatments of the first derivative, standard normal variate transformation, and multiplicative scatter correction did not improve the prediction accuracy of REE compared with Savitzky-Golay smoothing. This study provides a simple and rapid method for determining REE in soil, particularly for La, Pr, Nd, Sm, and total light REE.

1. Introduction

The rare earth elements (REE), comprising 15 lanthanides (La–Lu), Sc, and Y, play a remarkably important role in high-technology and clean-energy products (Haque et al., 2014). However, REE have demonstrated potential adverse effects on the functions of blood, bone, brain, lung, and liver in the human body (Rim et al., 2013) and thus are considered emerging pollutants (Brioschi et al., 2013). Nevertheless, the attention paid to the environmental and health risks of REE in soil is comparatively less than that given to heavy metals, such as Cd, Hg, Pb, Cr, Ni, and Sn. In the earth's crust, REE are as abundant as Cu, Pb, and Zn and are more abundant than Sn, Co, Ag, and Hg (Šmuc et al., 2012). Excessive REE in the soil mainly originate from the intensive use of REE-enriched fertilizers or pollutants during the mining and processing of REE, although parent materials also play an important role. For instance, in Australia, phosphate fertilizers were shown to contain 45.2 mg La kg⁻¹ and 61.0 mg Ce kg⁻¹, and in China, 11,000 tons of REE-bearing microelement fertilizers were applied to 6.5 million ha of land in 2001 (Hu et al., 2006). In addition, elevated contents of total

REE have been observed in agricultural soil surrounding REE mines and refining plants in China, e.g., 219.87 mg kg⁻¹ in Yucheng County (Mao et al., 2011), 542.00 mg kg⁻¹ in Ganzhou City (Gao et al., 2001), and 284.07 mg kg⁻¹ in Baotou City (Xu et al., 2011), which are considerably higher than the soil background value of 187.6 mg kg⁻¹ (Wei et al., 1991). Consequently, REE are enriched in vegetation and animals, resulting in accumulation in the human body through the food chain (Li et al., 2014). REE in human blood have been found to be significantly correlated with those in soil near residential areas (Li et al., 2013). Therefore, quantification of REE in soil is essential to protecting humans from environmental exposure.

However, determining REE is a challenging task due to their similar chemical properties (Verma et al., 2002). Inductively coupled plasma-mass spectrometry (ICP-MS) and emission spectrometry (ICP-ES), neutron activation analysis (NAA), and X-ray fluorescence (XRF) have been used to determine REE in diverse samples, including biological, environmental, and geological materials. For soil, ICP-MS, ICP-ES, and NAA have dominated in recent years (Zawisza et al., 2011). ICP-MS and ICP-ES can provide accurate and precise results with a low detection

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limit for soil samples, but they are time-consuming and expensive because of the complex sample preparation processes required, such as separation and pre-concentration. NAA directly determines REE with little sample preparation but requires more time and cost than ICP-MS and ICP-ES. Therefore, a rapid and inexpensive technique is urgently needed for determining REE in soil. Portable XRF devices can measure REE in soil in this manner. However, the spectral overlap of REE peaks, as well as the relatively high detection limit of Portable XRF, limits the use of this technology in soil to some extent. Therefore, wavelength-dispersive XRF spectrometers are applied in REE determination rather than portable energy-dispersive XRF instruments (Zawisza et al., 2011). In this case, sample preparations (e.g., pressing powder into pellets) should be done before determining REE. For details regarding techniques for determining REE, readers may refer to the review papers by Verma et al. (2002) and Zawisza et al. (2011).

Visible and near-infrared (Vis-NIR; 350–2500 nm) reflectance spectroscopy, a rapid and non-destructive analytical technique requiring little sample pretreatment, has been successfully used to determine soil properties, including soil organic carbon/matter (SOC/SOM), soil water content, total nitrogen, clay content, and some heavy metals (e.g., Hg) (Soriano-Disla et al., 2014; Stenberg et al., 2010; Wu et al., 2005). Determining soil properties via Vis-NIR is based either on their direct correlations with reflectance spectra (e.g., soil water) or on the indirect relationships with other soil properties (e.g., Ni estimated by its correlation with Fe instead of spectral reflectance) (Wu et al., 2010; Wu et al., 2007). Moreover, Vis-NIR reflectance spectra can simultaneously evaluate several soil properties (Ben-Dor and Banin, 1995; Viscarra Rossel et al., 2006). Until recently, little research focused on REE in soil, although the Vis-NIR reflectance spectra of REE-bearing minerals were reported five decades ago (Adams, 1965). This lack of attention may be attributed to the low REE content in soil (e.g., in China, the soil background value of total REE is 187.6 mg kg^{-1}); additionally, the spectral features of REE are vulnerable to being masked by those of SOM, soil water, and iron oxides.

The absorption features of most REE in Vis-NIR reflectance spectra originate from the f-f electron transition of REE^{3+} (Adams, 1965; Hunt, 1977), which is similar to the d-d electron transition of Fe^{2+} and Fe^{3+} . However, the absorptions are sharp for REE and broad for Fe because the 4-f orbitals of REE are shielded from outer orbitals, which also reduces the effects of crystal fields when REE are in coordination stages, resulting in the relatively stable absorption features of REE (Clark, 1999). The spectral difference between REE and Fe can be observed based on the spectra of iron oxides (goethite and hematite) and REE oxides (neodymium oxide and samarium oxide) (Fig. 1). Turner et al. (2014) identified the absorption bands of REE in Vis-NIR reflectance spectra based on the measured spectra of REE-bearing minerals and previous studies, and the bulk of the absorption features can be attributed to Nd^{3+} , Pr^{3+} , Sm^{3+} , and Eu^{3+} , mainly located in the region $< 1000 \text{ nm}$. Neave et al. (2016) reported that the absorption features of Nd were detected at wavelengths centered at 583, 744, 802, and 871 nm in minerals and rocks when the Nd concentration $> 1000 \text{ mg kg}^{-1}$, and in aqueous solution, Dai et al. (2013) observed the well-developed features of REE when total REE $> 75 \text{ mg L}^{-1}$. However, these features can hardly be detected in the spectrum of soil with total REE as high as $1624.5 \text{ mg kg}^{-1}$ (Fig. 1). In contrast, the features associated with clay minerals (montmorillonite and kaolinite) and iron oxides (goethite and hematite) are distinct in the spectrum (Fig. 1).

The absorption features of REE in Vis-NIR reflectance spectra have been used for mapping REE deposits (Boesche et al., 2015) and for evaluating the grade of REE ores (Turner, 2015) using imaging spectroscopy. Besides, Peralta-Zamora et al. (1997) and Rodionova et al. (2015) determined REE in acid solutions using absorption spectra obtained by spectrophotometers, in which the spectra ranged from 290 to 800 nm and from 200 to 1000 nm, respectively. Recently, some studies have reported the feasibility of Vis-NIR reflectance spectroscopy for determining REE contents in minerals (Neave et al., 2016) or in ore

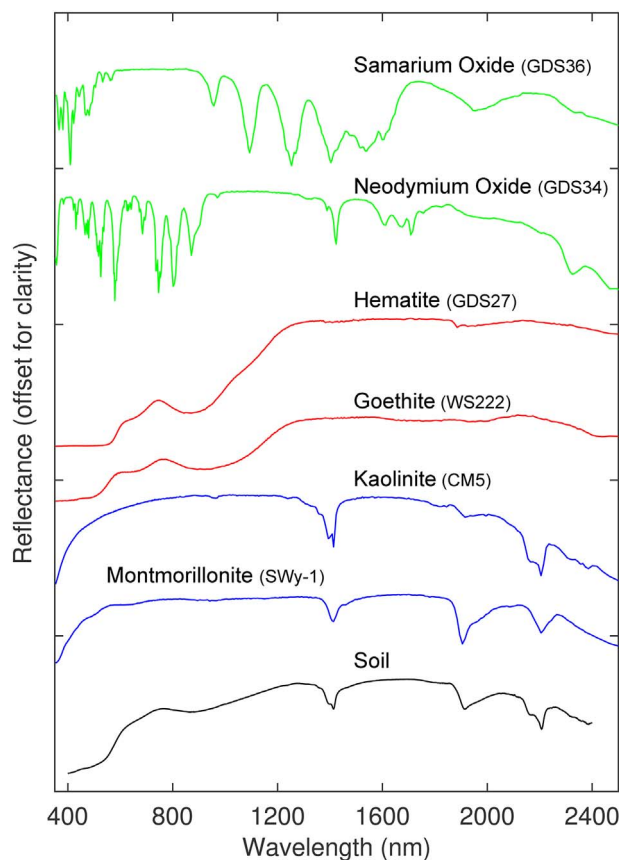


Fig. 1. Reflectance spectra (offset for clarity) of clay minerals (blue lines; montmorillonite and kaolinite), iron oxides (red lines; goethite and hematite), rare earth oxides (green lines; neodymium oxide and samarium oxide), and soil (black line). All spectra are sourced from the USGS spectral library (Clark et al., 2007) and limited to the range of 350 to 2500 nm, apart from the soil spectrum obtained from the collected soil samples in this study with the highest content of total rare earth elements ($1624.5 \text{ mg kg}^{-1}$). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

leachate solutions and contaminated stream water (Dai et al., 2013), based on the spectral absorption depth/area associated with REE. These studies provide the possibility of determining REE in soil by Vis-NIR reflectance spectroscopy. However, to the best of our knowledge, this approach has not been previously applied to determine REE in soil.

Therefore, the objective of this study was to investigate the potential of Vis-NIR reflectance spectroscopy as a novel tool for determining REE in soil, coupled with a chemometric method, i.e., partial least squares regression (PLSR). Specifically, the soil samples collected near REE mines were simply prepared by air-drying and grinding for spectral measurement. In addition to the full spectral range of 400–2400 nm, the spectra within 400–1000 nm were separately used to determine REE in soil because the spectral features of REE mainly appear in this region. The effect of spectral pretreatments on Vis-NIR determinations of REE was also investigated.

2. Materials and methods

2.1. Study area and sample collection

The study area ($\sim 26 \text{ km}^2$) (Fig. 2) is located in Anyuan County, Ganzhou City, Jiangxi Province, in south China—where low hills are widely distributed—which is known for REE-bearing lateritic ion-adsorption clays mainly dispersed in the upper parts of the hills. Over the past three decades, REE have been recovered from the ion-adsorption clays by leaching and precipitating processes using open-pit techniques, resulting in serious vegetation destruction, soil erosion, and soil and

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